HIGH-NITROGEN COMPOUNDS FOR USE IN LOW-EROSIVITY GUN PROPELLANTS

Thomas M. Klapötke* and Jörg Stierstorfer

Ludwig-Maximilian University Munich, Department of Chemistry and Biochemistry, Energetic Materials Research, 81377 Munich (Germany),
E-mail: tmk@cup.uni-muenchen.de, Fax: + 49 89 2180 77492

ABSTRACT

Nitrogen rich compounds are suitable as ingredients in low smoke propellant charges. Several high-N energetic materials are presented which are based on tetrazoles. Tetrazoles are an unique class of compounds, since they combine a high nitrogen content and a high heat of formation with good thermal and kinetic stabilities due to their aromatic ring system. The reaction of 5-azidotetrazole with hydrazine yields hydrazinium 5-azidotetrazolate (**1**), which is the tetrazole salt with the highest nitrogen content (88.1 %) reported, yet. In addition ammonium and aminoguanidinium 5-azidoterazolate were synthesized and characterized. The detonation and propulsion parameter were calculated using the EXPLO5 program. In addition several outperforming tetrazole derivatives (N% > 80 %), which are currently under our investigation as additives in propellant charges, are presented. Using the heats of formation and the X-ray densities, the detonation parameter of hydrazinium 5-aminotetrazole, 5,5'-bis(1*H*-tetrazolyl)-hydrazine, 5,5'-bis(1*H*-tetrazolyl)-amine, 5,5'-bis(1-methyltetrazolyl)-triazene, 1,5-bistetrazole and its ammonium salt were calculated.

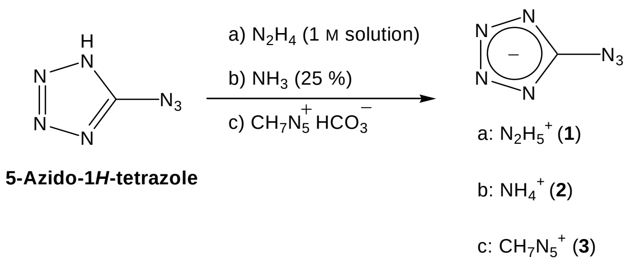
1. INTRODUCTION

Several approaches are being pursued to provide new energetic materials to meet the challenges of the future.[1] Recent modeling and testing has shown that the presence of high concentrations of nitrogen species in the combustion products of propellants can reduce gun barrel erosion by promoting the formation of iron nitride rather than iron carbide on the interior surface of the barrel. Thus compounds such as hydrazinium azidotetrazolate (N = 88.1%) show promise for use in low-erosivity gun propellants.

Energetic materials are most commonly used in either high explosives (HE) or propellant formulations.[2] Whereas the performance of HEs can be related to heat of explosion (*Q*), detonation pressure (*p*) and detonation velocity (*D*), the performance of rocket/missile propellants is best characterized by their specific impulse (I_{sp}). Moreover, for gun propellants, erosivity is an additional concern and lower reaction temperatures and a high N_2/CO ratio of the reaction gases are desirable.[3] Whereas single-base propellants are used in all guns from pistols to artillery weapons, the more powerful (see I_{sp}) double-base propellants are commonly used in pistols and mortars. The disadvantage of double-base propellants is the excessive erosion of the gun barrel (see N_2/CO ratio) by the much higher flame temperatures, and the presence of a muzzle flash (fuel-air explosion of the combustion products). In order to reduce erosion and muzzle flash, triple-base propellants with up to 50% nitroguanidine are used in tank guns, large calibre guns and naval guns. However, the performance of triple-base propellants is lower than that of double-base propellants.Here we report on three highly energetic salts of the CN_7^- anion which represent the highest N-content ever reported for a tetrazolium salt. In addition we present several other high-N compounds which are currently under investigation.

2. RESULTS AND DISCUSSION

For the first time, we succeeded in an appropriate synthesis and characterization of salts containing the nitrogen-rich CN_7^- anion. The investigated CN_7^- is a highly energetic and endothermic anion resulting in salts with high sensitivities but good thermal stabilities. In this work we present three examples combining the CN_7^- anion with the nitrogen-rich cations hydrazinium, ammonium and aminoguanidinium. These compounds have been synthesized in good yields according to scheme 1.



Scheme 1. Synthesis of nitrogen-rich salts containing the CN_7^- anion.

The energetic salts hydrazinium (N_2H_5, **1**), ammonium (NH_4, **2**) and aminoguanidinium (AG, **3**) 5-azidotetrazolate were characterized by single X-ray diffraction (Figure 1). In addition, the sensitivities and

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the energetic properties were tested experimentally and computationally.

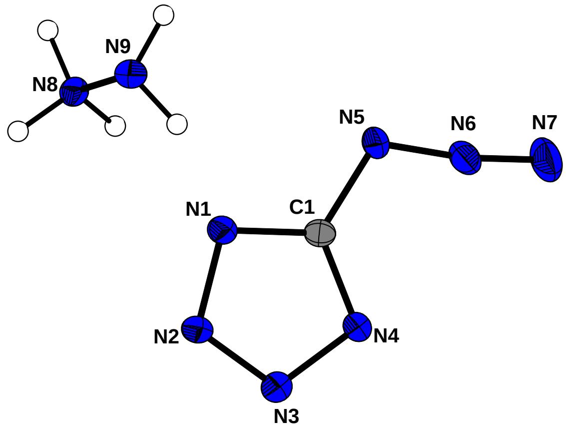


Figure 1. Molecular structure of **1**. Thermal ellipsoids reperesent the 50 % propability level.

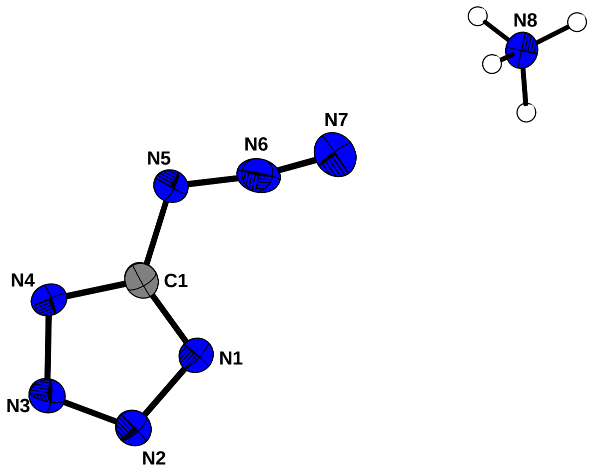


Figure 2. Molecular structure of **2**.

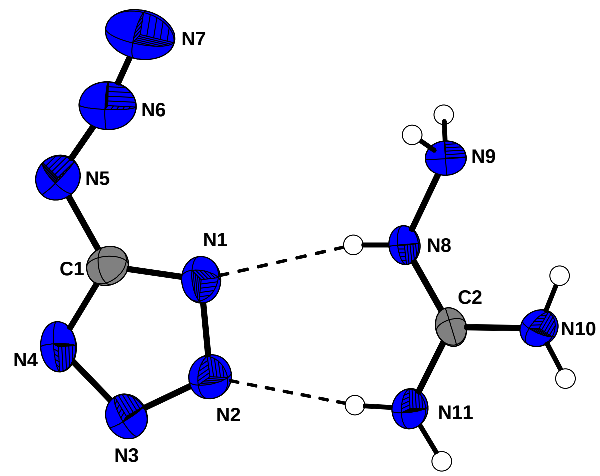


Figure 3. Molecular structure of **3**.

The energetic and thermodynamic properties of **1** - **3** are summarized in Table 1. Although **1** and **2** are members of the TOP 10 molecules carrying the highest nitrogen content, both are kinetically stable and show promising high decomposition temperatures. The enthalpies and free energies of formation were calculated using the CBS-4M method [4] combined with the atomization energy procedure.[5] The calculated detonation parameters of **1** and **2** exceed those observed for RDX.[6]

More importantly, the specific impulses and the molar N_2/CO ratios for the combustion gases are the relevant numbers for the characterization of propellants and general (I_{sp}) and gun-propellants in particular (N_2/CO). Table 2 summarizes the computed isobaric combustion temperatures ($T_{c,}$ the lower the better), the specific impulses (I_{sp}) and the molar N_2/CO ratios for **1**, **2**, **3**, a 60:40 mixture of **1** with ADN and three typical conventional gun-propellants (single-, double-, triple-base) and a typical 70:30 solid booster mixture of AP/Al.

Table 1. Pysico-chemical properties of **1 - 3** in comparison with RDX.

	1	**2**	**3**	**RDX**
Impact sensitivity [a] / J	1	1	1	7
Friction sensitivity [b] / N	5	5	7	120
Electros. discharge sens. [c] / mJ	5	10	40	> 150
N-content / %	88.1	87.5	83.2	37.8
T_{dec} [d] / °C	136	157	159	ca. 213
calculated values (EXPLO5 code)				
$-Q_{ex}$ [e] / kJ kg^{-1}	5592	4829	4193	6043
T_{ex} [f] / K	3813	3498	3052	4321
$p_{C\text{-}J}$ [g] / kbar	306	287	241	346
D [h] / m s^{-1}	9231	8917	8424	8750

[a] BAM drophammer; [b] BAM friction tester; [c] OZM small scale electrical discharge tester; [d] Linseis PT10 DSC (5 deg min^{-1}); [e] heat of detonation, [f] detonation temperature, [g] detonation pressure; [h] detonation velocity.

Table 2. Computed propulsion relevant parameters.

	isobaric comb. temp., T_C / K	I_{sp} / s	molar N_2/CO ratio
NC[a]	2712	200	0.31
NC/ NG[b] (50:50)	3145	211	0.63
NC /NG / NQ[c] (25:25:50)	2640	203	1.28
1	2910	230	85.5
2	2686	216	84.6
3	2201	199	80.3
1/ADN[d] (60:40)	3082	231	6.7
AP[e]/AL[f] (70:30)	4034	209	---

[a] NC, nitrocellulose; [b] NG, nitroglycerine; [c] NQ, nitroguanidine.[d] ADN, ammonium dinitramide; [e] ammonium perchlorate, [f] aluminum.

The disadvantage of double-base propellants is the excessive erosion of the gun barrel (see N_2/CO ratio) by the much higher flame temperatures, and the presence of a muzzle flash (fuel-air explosion of the combustion products). In order to reduce erosion and muzzle flash, triple-base propellants with up to 50% nitroguanidine are used in tank guns, large caliber guns and naval guns. However, the performance of triple-base propellants is lower than that of double-base propellants. Compounds **1** - **3** show relatively low com-bustion temperatures (comparable to single- and triple-base propellants), with excellent molar N_2/CO ratios (which are usually 0.5 – 1.0 for conventional propellants). A 60:40 mixture of **1** with ADN possesses a calculated I_{sp} of ca. 20 s higher than that of a commonly used AP/Al booster mixture.

Unfortunately the described compounds are highly sensitive towards external effects. Therefore several other compounds (Chart 1) with a nitrogen content above 80 % are in our focus as ingredients in propellant charges.

In the following selected examples of Chart 1 are further described.

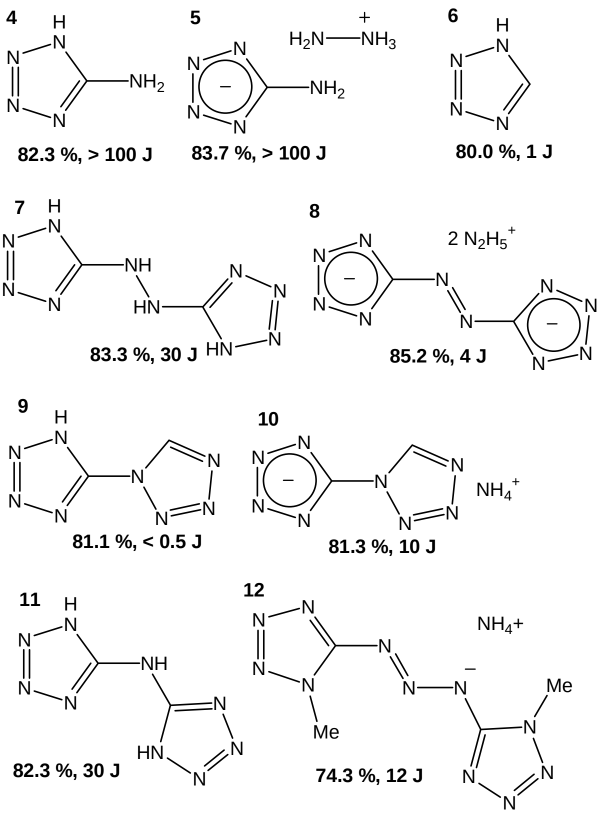


Chart 1. Tetrazole derivatives with a nitrogen content above 80 % and their sensitivity towards impact. **4**: 5-amino-1*H*-tetrazole, **5**: Hydrazinium 5-aminotetrazolate, **6**: 1*H*-tetrazole, **7**: BTH, bis(1*H*-tetrazolyl)hydrazine, **8**: hydrazinium 5,5'-azotetrazolate,[7] **9:** 1,5-bistetrazole, **10**: ammonium 1,5-bistetrazolate, **11**: H_2bta, 5,5'-bis(1*H*-tetrazolyl)amine, **12**: dihydrazinium 5,5'-bis(1*H*-tetrazolyl)amine.

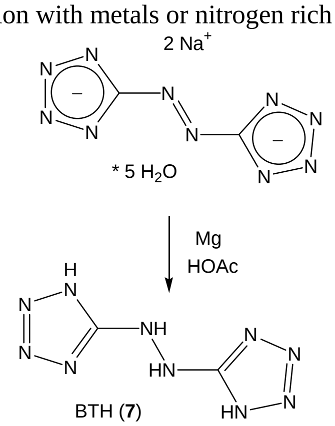
Hydrazinium 5-aminotetrazolate

Hydrazinium 5-aminotetrazolate (**5**) [8] was synthesized via two facile routes. Both the reaction of 5-amino-1*H*-tetrazole (**4**) with hydrazine hydrate in aqueous solution and the reaction of **1** with diluted hydrazine solution in THF yield **5** in excellent purities and yields. The heat of formation was calculated (CMS-4M) using the atomization method to be 373 kJ mol^{-1}. With this value and the X-ray density several detonation parameter (heats of explosion, detonation pressure, detonation velocity, explosion temperature) were calculated by the EXPLO5 computer software. An incredible high value (9516 m s^{-1}) was obtained for the detonation velocity.

Therefore experimentally tests to determine the velocity of detonation were performed. Initiation was achieved with an electrically ignited (40 V, 5 A) PETN-SAcN detonator (1 g PETN, 0.2 g silver acetylide nitrate). Although initiation of the detonator and the booster charge were achieved without any problems, compound **5** could not be initiated using this set-up. This clearly shows the insensitivity of compound **5** towards initiation even when a PETN booster charge was used. The use of **5** in solid propellant compositions was calculated and tested in combination with oxidizers, e.g. ammonium dinitramide which show promising results.

5,5'-Bis(tetrazolyl)hydrazine

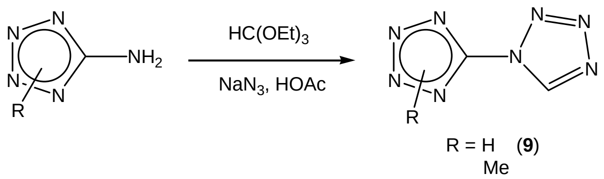
Reduction of 5,5'-azotetrazolates to 5,5'-bis(tetrazolyl)hydrazine (**BTH**, **7**) using magnesium was also described by J. Thiele.[9] BTH is stable towards temperatures above 200 °C and shows promising detonation and propulsion parameter.[10] It can also be deprotonated forming 5,5'-*bis*(tetrazolato)-hydrazine (**8**) in combination with metals or nitrogen rich cations.



Scheme 2. Formation of 5,5'-bistetrazolyl-hydrazine (BTH)

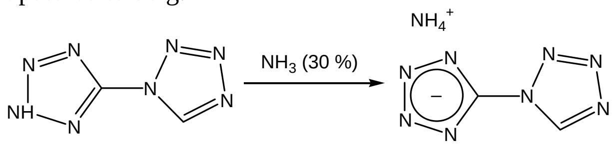
1,5-Bistetrazoles

Our ongoing work on 1,5-bistetrazoles [11] is very profitable, thus several new derivatives have been created and characterized. The following scheme shows a general protocol of syntheses of 1,5-bistetrazoles starting from 5-aminotetrazoles.



Scheme 3. Syntheses of 1,5-bistetrazoles

Unfortunately **9** decomposes already at 145 °C. In addition it can be only handled as its monohydrate. The waterfree compound is extremely explosive and sensitive towards friction and impact. With regards to develop new thermal stable high-N propellants, the ammonium salt of 1,5-bistetrazole (**10**),[12] shows better characteristics ($T_{dec.}$: 240 °C) and was successfully upscaled to 50 g.



Scheme 4. Synthesis of ammonium 1,5-bistetrazolate (**10**)

Fortunately we succeeded in obtaining single crystals of **9***H_2O as well as of **10**. The molecular structures of **9** and **10** are depicted in Fig. 4 and 5.

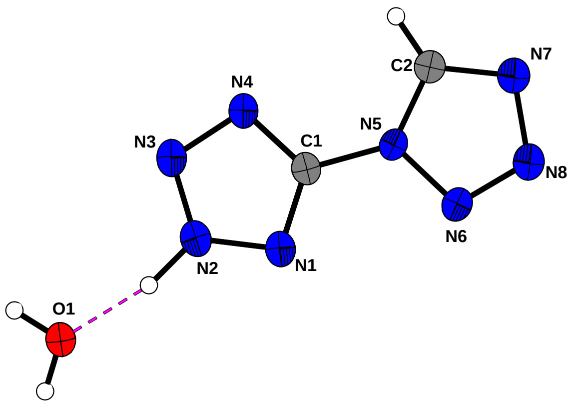


Figure 4. Molecular structure of **9***H_2O. Thermal ellipsoids reperesent the 50 % propability level.

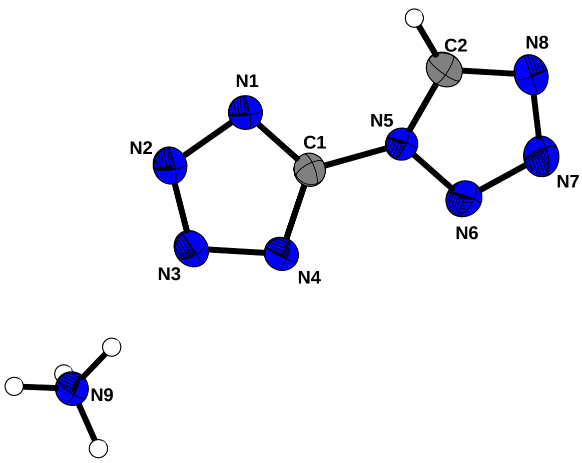
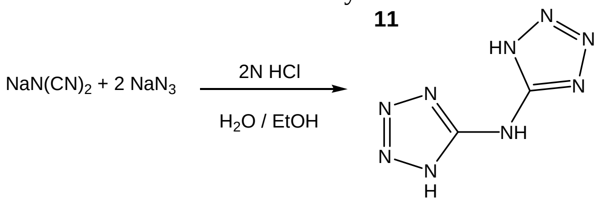


Figure 5. Molecular structure of **10**. Thermal ellipsoids reperesent the 50 % propability level.

Bistetrazolylamines

Bistetrazolylamines, especially water free H_2bta (**11**),[13] are a valuable class of energetic compounds, due to their high nitrogen content, their high decomposition temperatures, the low sensitivities and their ease of preparing. The following scheme gives an overview about the most facile synthesis of **11**.



Scheme 5. Synthesis of H_2bta (**11**)

In 2008 we succeeded to obtain single crystal of low soluble compound **11** as well as its monohydrate. Interestingly in water free **11** the protons are not located at the positions expected. A comparison of the molecular structures of 11 and 11*H_2O can be found in Fig. 4 and 5.

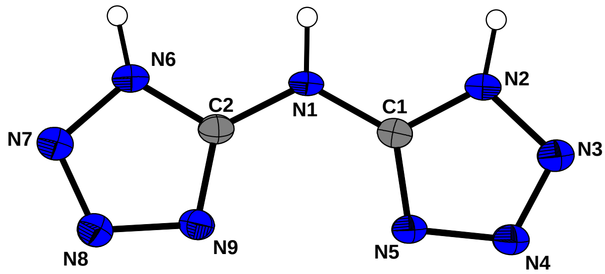


Figure 4. Molecular structure of **11**. Thermal ellipsoids reperesent the 50 % propability level.

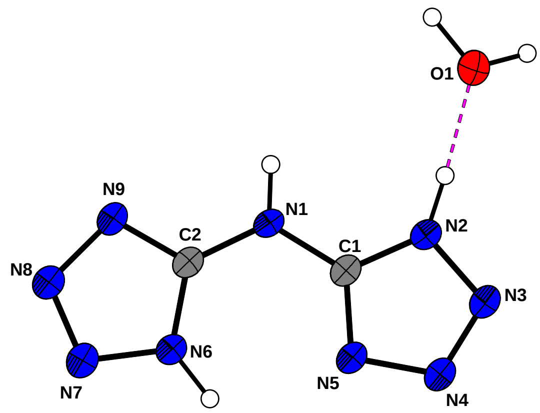
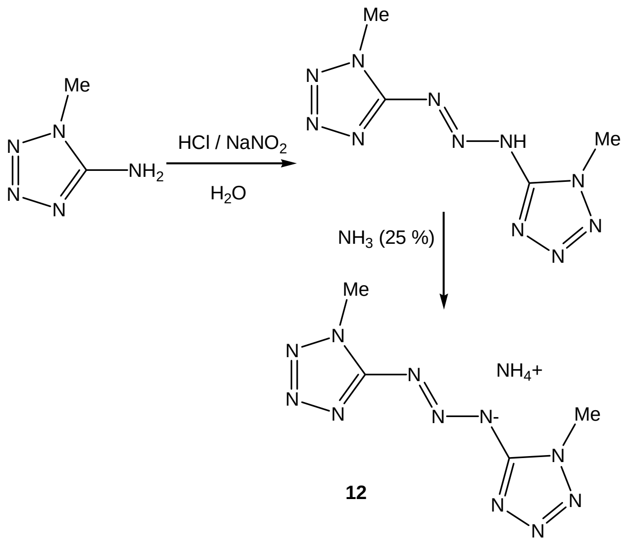


Figure 5. Molecular structure of **11***H_2O. Thermal ellipsoids reperesent the 50 % propability level.

Bistetrazolyltriazenes

Bistetrazolyltriazenes are also a very promising class of new N-rich energetic materials due to their high thermal stability.[14] They can be easily obtained by diazotation of 5-aminotetrazole derivatives using half an equivalent of “NO_2^-“. Scheme 6 presents the synthesis of ammonium 5,5’-*bis*(1-methyltetrazolyl)triazene (**12**).



Scheme 6. Synthesis of ammonium 5,5'-bis(1-methyltetrazolyl)triazene.

A formulation of **6** with ADN (**6**: ADN = 30:70) shows promising calculated propulsion parameter using a chamber pressure of 70 bar.. The combustion temperature (3037 K, between single and double based propellants), with an excellent molar N_2/CO ratio of 5.82 (which are usually 0.5 for conventional propellants). The computed specific impulse of 251 s for such a mixture make a possible application of **6** as promising energetic component in erosion-reduced gun propellants very interesting.

In the following Table3 a comparison of the computed detonation parameter of **5**, **6**, **7**, **9**, **10**, **11** and **12** are summarized. All calculations have been carried out using the EXPO5 software.[15]

Interestingly compound **5**, which shows the best detonation parameter is insensitive and can not be detonated.

Table 3.Calculated detonation parameters for compound **5**, **6**, **7**, **9**, **10**, **11** and **12**

	5	**6**	**7**	**9**	**10**	**11**	**12**
$T_{Dec.}$	186	188	208	145	240	250	236
ρ / g cm^{-3}	1.55	1.53	1.84	1.67	1.57	1.86	1.60
N / %	83.7	80.0	83.3	81.1	81.3	82.3	74.3
Ω / %	-75.1	-68.52	-57.1	-51.2	-67.0	-57.5	-92.0
Q_v / kJ kg^{-1}	-4295	-3941	-2950	-4955	-4228	-4537	-3714
T_{ex} / K	2759	3047	2539	3694	3147	3449	2626
P / kbar	296	210	277	273	246	343	248
D / m s^{-1}	9516	7813	8523	8406	8382	9120	8484
V_0 / L kg^{-1}	959	785	783	784	812	753	816

3. CONCLUSIONS

Several new tetrazole derivatives with a nitrogen content above 80 % have been synthesized, which can be used due to their large positive heat of formation as energetic materials in high explosives as well as fuels in propellant charges. Especially in the matter case smokeless combustible materials are desired to reduce the erosion in gun weapons as well as the signature of missiles. Next to a good performance, the thermal stability, a suitable synthetic procedure and low sensitivities are desired. These criterias strongly depends on the constitution of N-rich molecules and can not correlated with the nitrogen content. Aminoguanidinium 5-azidotetrazolate (**3**, N% = 83.2 %) as well as hydrazinium 5-aminoterazolate (**5**, N% = 83.7 %) have similar nitrogen contents, but show significantly different energetic behaviors. **3** is a highly sensitive primary explosive, while **5** can not be detonated also be using strong primer charges. However, 5 can be used as fuel in solid propellants, when mixed with a suitable oxidizer, e.g. ammonium dinitramide. Hydrazinium 5-azidotetrazolate is the tetrazole salts with the highest nitrogen content and the first structural characterized compound containing the CN_7^- anion. In addition several bistetrazole derivatives are presented. Especially ammonium 1,5-bistetrazolate (**10**), 5,5'-bistetrazolylamine (**11**) and 5,5'-bis(1-methyl-tetrazolyl)triazenate (**12**) combine outstanding stabilities towards temperature and high heats of formation with low sensitivities towards impact, friction and electrical discharge.

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